Oxidative Additions of Coordinated Ligands at Unsaturated Molybdenum and Tungsten Diphosphine-Bridged Carbonyl Dimers. 2. Decarbonylation Reactions of $[Mo_2(\eta^5\text{-}C_5H_4R)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$ (R = H, Me)

Gema García, M. Esther García, Sonia Melón, Víctor Riera, and Miguel A. Ruiz*

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain

Fernando Villafañe

Departamento de Química Inorgánica, Universidad de Valladolid, E-47005 Valladolid, Spain

Received August 20, 1996[⊗]

Decarbonylation of the dimolybdenum complexes $[Mo_2(\eta^5\text{-}C_5H_4R)_2(CO)_4(\mu\text{-dppm})]$ (R = H, Me, dppm = $Ph_2PCH_2PPh_2$) occurs readily upon heating in tetrahydrofuran or toluene solution to afford with good yield the phosphido complexes $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$, which arise from an irreversible P−C(sp^3) bond cleavage in the backbone of the dppm ligand. Other minor products in these reactions are the oxo complexes $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}CH_2PPh_2)(O)(\mu\text{-}PPh_2)(CO)]$, which are formed by the action of oxygen on the former dicarbonyl compounds, and the triply-bonded complexes $[Mo_2(\eta^5\text{-}C_5H_4R)_2(CO)_2(\mu\text{-dppm})]$, in which the dppm ligand remains intact. By contrast, photochemical decarbonylation of the parent tetracarbonyl complexes at 10 °C yields the triply-bonded dicarbonyls as major products, along with a small amount of the monocarbonyl complexes $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-CO})]$. Separate experiments show that the latter compounds are formed from $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ under photolytic conditions, this reaction being reversible. Thus it is concluded that the P−C(sp^3) cleavage of the dppm ligand is fairly well suppressed at ambient temperatures or below. The reactions of all the above unsaturated species with CN^tBu proceed rapidly at room temperature. In this way, the new isocyanide derivatives $[Mo_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(\mu\text{-CO})(CO)]$, $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(CO)]$, and $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-dppm})]$ have been prepared. All of them are formed in good yields as single isomers but have a rather low stability. Reaction of the monocarbonyl derivative with atmospheric oxygen gives the oxo complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2PPh_2)(\mu\text{-O})(\mu\text{-}OPPh_2)(CN^tBu)(CO)]$, which is also obtained as a single isomer. In marked contrast to their ditungsten analogues, the isocyanide-bridged compounds $[Mo_2(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-dppm})]$ do not experience C−H bond cleavages in their cyclopentadienylic rings to a significant extent.

Introduction

In the first part of this series we have shown that decarbonylation of the ditungsten complex $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ (Cp = η^5-C_5H_5; dppm = $Ph_2PCH_2PPh_2$) leads mainly to the triply-bonded species $[W_2Cp_2(CO)_2(\mu\text{-dppm})]$.[1] This can be accomplished either thermally or photochemically and occurs *via* the hydrido cyclopentadienylidene complex $[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-H})(CO)_3(\mu\text{-dppm})]$, a product derived from the intramolecular cleavage of a C−H bond in the cyclopentadienyl ligand, which turns out to be reversible. The above results are in marked contrast with our preliminary decarbonylation studies on the related dimolybdenum complex $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$ (**1a**), which showed that P−C(sp^3) bond cleavage of the dppm ligand was the dominant process under thermolytic conditions, this leading to the unsaturated species $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (**2a**).[2] In view of the general interest of C−P[3] and C−H[4] activation processes we decided to examine in more detail the decarbonylation reactions of the dimolybdenum compound **1a** and to extend these studies to its methylcyclopentadienyl analogue $[Mo_2Cp'_2(CO)_4(\mu\text{-dppm})]$ (**1b**) (Cp′ = η^5-C_5H_4Me).

Results and Discussion

Starting Substrates. The synthesis of compound **1a** has been previously described.[5] The methylcyclopen-

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

(1) (a) Part 1: Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L. R.; Bois, C. *Organometallics*, in press. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3786.

(2) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *375*, C23.

(3) (a) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. (b) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(4) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 295. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (d) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (f) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(5) Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854.

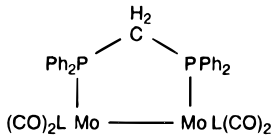
S0276-7333(96)00715-7 CCC: $14.00

Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Compounds

compd	ν_{st}(CO)[a]/cm^{-1}	δ(P)[b]	J_{PP}
$[Mo_2Cp'_2(CO)_4(\mu\text{-dppm})]$ (**1b**)	1842 (m), 1822 (ms)	46.5 (br, isomer *A*)	
	1913 (ms), 1874 (vs)[c]	34.8 (br, isomer *B*)[d]	
$[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (**2a**)	1835 (m, sh), 1807 (s)[c]	92.1, 46.8[e]	16
$[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (**2b**)	1833 (m, sh), 1796 (s)[c]	94.0, 46.6[f]	16
$[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(O)(\mu\text{-}PPh_2)(CO)]$ (**3b**)	1787 (s)[c,g]	198.8, 39.6[e]	3
$[Mo_2Cp_2(CO)_2(\mu\text{-dppm})]$ (**4a**)	1739 (s)	57.9	
$[Mo_2Cp'_2(CO)_2(\mu\text{-dppm})]$ (**4b**)	1735 (s)	58.0	
$[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)]$ (**5a**)	1674 (s)	206.0, 20.4[f]	16
$[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)]$ (**5b**)	1669 (s)	207.1, 21.7[e]	16
$[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-dppm})]$ (**6a**)	1825 (s), 1788 (vs)[h]	53.5, 37.7[f]	84
$[Mo_2Cp'_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-dppm})]$ (**6b**)	1825 (s), 1788 (vs)[i]	52.4, 35.5	84
$[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CN^tBu)(CO)_2(\eta^1\text{-dppm})]$ (**7**)	1836 (s), 1805 (vs)	72.8, −25.0 (isomer *A*)	84
		72.5, −25.1 (isomer *B*)[k]	83
$[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(\mu\text{-}CO)(CO)]$ (**8**)	1833 (s, br), 1685 (m)[l]	104.8, 67.5[m]	2
$[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(CO)]$ (**9**)	1760 (vs)[n]	103.4, 58.7[o]	8
$[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}OPPh_2)(\mu\text{-O})(CN^tBu)(CO)]$ (**10**)	1815 (vs)[c,p]	107.6, 58.9	187

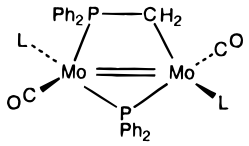
[a] Recorded in THF solution unless otherwise stated. [b] Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; *J* in hertz. [c] Toluene solution. [d] Recorded at 161.98 MHz; ratio *B*:*A* *ca.* 5; this ratio increases to *ca.* 20 at 233 K. [e] C_6D_6 solution. [f] Toluene-d_8 solution. [g] ν_{st}(Mo−O) = 907 cm^{-1} in KBr disk. [h] ν_{st}(CN) = 1666 (w), 1636 cm^{-1} (w). [i] Dichloromethane solution; ν_{st}(CN) = 1655 (w), 1636 (w). [j] ν_{st}(CN) = 2120 (w), 1651 (w), 1619 cm^{-1} (w). [k] Ratio *A*:*B* *ca.* 1. [l] ν_{st}(CN) = 2130 (s). [m] 253 K. [n] ν_{st}(CN) = 2040 cm^{-1} (s). [o] 213 K. [p] ν_{st}(CN) = 2112 cm^{-1} (s).

Chart 1

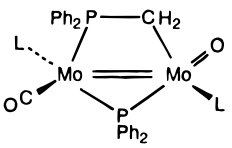


1a (L= η^5-C_5H_5 or Cp)
1b (L= η^5-C_5H_4Me or Cp′)

Chart 2



2a,b



3a,b

tadienyl complex **1b** is analogously prepared by addition of dppm to the triply-bonded dimer $[Mo_2Cp'_2(CO)_4]$. As found for **1a**, complex **1b** displays two isomers in solution (labeled *A* and *B*, Table 1), with their ratio being temperature and solvent dependent. Because of the relatively fast exchange between isomers (on the NMR time scale) sharp NMR resonances for **1b** could only be obtained at low temperature, where isomer *B* is the dominant species present (ratio *B*:*A* *ca.* 10 at 253 K in CD_2Cl_2 solution). Its ^1H NMR spectrum showed the chemical equivalence of the methylenic protons of the dppm ligand, in agreement with the data previously obtained for $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$.[1] Thus we conclude that, contrary to our earlier proposal for **1a**,[5] and in agreement with that of Azam et *al.* on the same complex,[6] the structures of isomers *A* and *B* in solution are adequately represented by those determined crystallographically for $[Mo_2Cp_2(CO)_4(\mu\text{-}H^tBuPCH_2P^tBuH)]$[7] (isomer *A*) and for **1a**[6] (isomer *B*) (Chart 1).

The presence of the methylcyclopentadienyl ligand in **1b** increases both the electron density and steric hindrance at the dimolybdenum center, when compared with the cyclopentadienyl complex **1a**. The former effect is reflected in the average ν_{st}(CO) frequencies, decreasing in toluene solution from 1869 cm^{-1} (**1a**) to 1860 cm^{-1} (**1b**), the latter value being the same as that found for the ditungsten complex $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$.[1] As will be seen later, this does not translate into similar chemical behaviors for **1b** and the ditungsten complex. On the other hand, changes in the steric hindrance at the dimetal center are expected due to the higher cone angle of the methylcyclopentadienyl ligand, relative to the unsubstituted ring, the difference being estimated as *ca.* 10°.[8] The above modifications have clear structural consequences. For example, the ratio between isomers *B* and *A* in CD_2Cl_2 solution at 291 K increases from *ca.* 2 (for **1a**) to *ca.* 5 (for **1b**), a change that can be mostly attributed to steric factors by recalling that the *B*:*A* isomer ratio for the ditungsten complex $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ is *ca.* 0.5 under the same conditions. However, in spite of this marked structural effect, the presence of the methylcyclopentadienyl ligand induces only a quite modest influence on the decarbonylation reactions of these dimetallic substrates, as will be next discussed.

Thermal Decarbonylation of Compounds 1. Complex **1a** is readily decarbonylated in tetrahydrofuran at 60 °C to give the unsaturated complex $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (**2a**) (Chart 2) in high yield, along with trace amounts of the oxo compound $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(O)(\mu\text{-}PPh_2)(CO)]$ (**3a**) and the triply-bonded complex $[Mo_2Cp_2(CO)_2(\mu\text{-dppm})]$ (**4a**). Compound **3a** is probably formed during manipulation of the reaction mixture. This follows from the previous observation that **3a** is a major product in the reaction of **2a** with molecular oxygen.[9] On the other hand, the relative amounts between isomers **2a** and **4a** could not be significantly modified by changing the reaction conditions (solvent, temperature, etc.). Moreover, pure samples of compounds **2a** or **4a** did not show noticeable transformations upon heating under the above conditions.

The methylcyclopentadienyl complex **1b** behaves analogously, affording the P−C cleavage product **2b** in high

(6) Azam, K. A.; Deeming, A. J.; Felix, M. S. B.; Bates, P. A.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1793.
(7) Brauer, D. J.; Hasselkuss, G.; Stelzer, O. *J. Organomet. Chem.* **1987**, *321*, 339.
(8) Coville, N. J.; du Plooy, K. E.; Pickl, W. *Coord. Chem. Rev.* **1992**, *116*, 1.
(9) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *Organometallics* **1993**, *12*, 124.

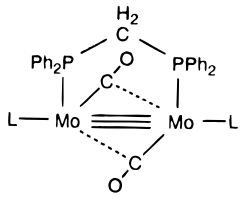
yield, along with small amounts of **3b** and **4b**. However, IR monitoring of the reaction (either in toluene or THF) shows in this case additional ν_{st}(CO) bands at 1969, 1908, 1890, 1780, and 1743 cm^{-1}, which can be attributed to [MoCp′$(CO)_2$(dppm)][MoCp′$(CO)_3$] by comparison to its cyclopentadienyl analogue.[5] The formation of this side product, not observed during decarbonylation of **1a**, might reflect the increase in the steric pressure at the dimetal center introduced by the methylcyclopentadienyl ligands.

Spectroscopic data for the oxo complex **3b** are entirely analogous to that for **3a**, which we have discussed previously in detail,[9] and need then no further comment. The structure has been confirmed through an X-ray study on the ditungsten analogue [$W_2Cp_2(\mu$-CH_2PPh_2)-(O)(μ-PPh_2)(CO)].[1] The proposed structure for the dicarbonyls **2** is based on that of the latter oxo complex, after replacing the terminal oxo ligand by a carbonyl. This results in a *trans* arrangement of both carbonyls in the molecule, relative to the average plane defined by the metal atoms and bridging ligands. In agreement with this proposal, the IR spectra of compounds **2** exhibit the ν_{st}(CO) pattern expected for such a relative arrangement (medium and strong intensities, in order of decreasing frequency).[10] The phosphinomethyl ligand in complexes **2** is characterized by a ^{31}P NMR resonance in a region similar to that of the dppm complexes **1**, while its CH_2 group gives characteristic low-field ^1H and ^{13}C NMR resonances, as expected from its coordination to a transition-metal atom. The phosphido ligands in compounds **2** give rise to a more deshielded resonance as expected.[11] The corresponding chemical shifts (*ca.* 90 ppm) are similar to that found for the isoelectronic bis(phosphido) complex [$Mo_2Cp_2(\mu$-$PPh_2)_2(CO)_2$].[12] Yet, these shifts can be considered somewhat low for a diphenylphosphido bridge at a metal−metal-bonded binuclear complex. Because of the unsaturated nature of compounds **2**, the intermetallic distance is expected to be short, thus leading to relatively low Mo−P−Mo bond angles. This in turn could cause a shielding effect on the ^{31}P resonance of the phosphido bridge, as it has been previously found for binuclear group 8 complexes.[11,13]

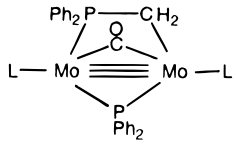
Photochemical Decarbonylation of Compounds 1. Compounds **1a**,**b** are slowly decarbonylated by the action of UV light in tetrahydrofuran at 10 °C to give the triply-bonded dicarbonyl complexes **4a**,**b** in high yield, along with small amounts of the monocarbonyl species [$Mo_2L_2(\mu$-$CH_2PPh_2)(\mu$-$PPh_2)(\mu$-CO)] (**5a**, L = Cp; **5b**, L = Cp′). Noticeably, the dicarbonyl complexes **2** were completely absent in these reaction mixtures.

Separate experiments showed that compounds **4** and **5** arise from different reaction pathways. Thus, pure samples of compounds **4** gave no detectable amounts of the corresponding complexes **5** after prolonged exposure to the UV light. On the other hand, compounds **5** can be obtained almost quantitatively upon UV photolysis of the dicarbonyl compounds **2**. Moreover, the photochemical transformation from **2** to **5** was found to occur faster than that one from **1** to **4**. Thus it is concluded that, contrary to the thermolytic experiments, the photochemical decarbonylation of compounds **1** leads mainly to the dppm-bridged dicarbonyls **4** (Chart 3) and only to small amounts of the P−C cleavage products **2** which, being rapidly decarbonylated under the experimental conditions, are observed as their monocarbonyl derivatives **5**. From the above data it seems that formation of the P−C cleavage products (**2** or **5**) is fairly suppressed at low temperatures. However, full suppression of the P−C cleavage process could not be reached, because the photochemical decarbonylation of compounds **1** below 0 °C becomes too slow to be effective in a preparative sense.

Chart 3



4a,b



5a,b

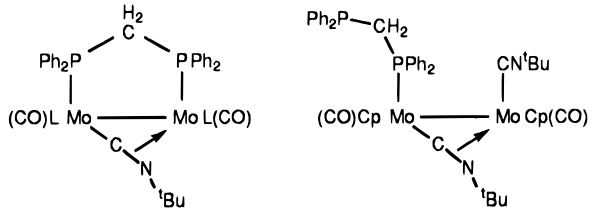
Spectroscopic data for compounds **4** indicate a close structural relationship to the ditungsten triply-bonded complex [$W_2Cp_2(CO)_2(\mu$-dppm)].[1] The crystal structure of the latter revealed the presence of linear semibridging carbonyls experiencing an incipient dynamic disorder, which in solution was observed in the form of a rapid scrambling of the carbonyl ligands between both metal centers. This seems to be also the case for the dimolybdenum compounds **4**, as far as the structure in solution is concerned. Thus, the IR spectra of complexes **4** display a single ν_{st}(CO) band at *ca.* 1740 cm^{-1} and a single ^{13}C NMR resonance for the carbonyl ligands at *ca.* 254 ppm (to be compared to 1730 cm^{-1} and 241 ppm for the ditungsten complex).

The structural characterization of the monocarbonyl complexes **5** is firmly supported on their spectroscopic data. The bridging nature of the single carbonyl ligand in these molecules is clearly indicated by their low ν_{st}-(CO) values (*ca.* 1670 cm^{-1}) and high ^{13}C NMR chemical shifts (*ca.* 305 ppm). The phosphinomethyl ligand gives rise to the expected ^{31}P, ^{13}C, or ^1H NMR resonances, not very different from those exhibited by their dicarbonyl precursors **2**. However, the ^{31}P NMR chemical shift of the phosphido group in compounds **5** (*ca.* 207 ppm) is *ca.* 110 ppm higher than those found for compounds **2**. The bis(phosphido) complex [$Mo_2Cp_2(\mu$-$PPh_2)_2(\mu$-CO)], which is isoelectronic to **5**, has been shown to display a similar ^{31}P NMR chemical shift (*ca.* 198 ppm) and a very short intermetallic distance (2.515-(2) Å).[12] Thus, the dramatic differences in the ^{31}P NMR shifts found for compounds **2** and **5** can be hardly explained only on the basis of geometrical grounds. Therefore, it is likely that the differences in the formal bond orders for the above species (double *vs* triple metal−metal bond) have a significant influence on the shielding of the phosphido group.

Reactions of Compounds 4 with CO and CN^{t}Bu. As we have said above, the formation of the triply-bonded complex [$W_2Cp_2(CO)_2(\mu$-dppm)] from [W_2Cp_2-$(CO)_4(\mu$-dppm)] proceeds through the hydrido cyclopen-

(10) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.
(11) Carty, A. J.; MacLaughin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 16.
(12) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.
(13) Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. *Inorg. Chem.* **1989**, *28*, 4120.

Chart 4



6a,b **7**

tadienylidene complex $[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-}dppm)]$. In the case of our dimolybdenum complexes, no intermediates were detected during the formation of dicarbonyls **4**. In an attempt to reach these presumed intermediates we examined the reactions of **4** with CO and CN^tBu.

Complexes **4** are rapidly carbonylated at room temperature or below to regenerate the parent tetracarbonyls **1**. Unfortunately, no intermediates were detected in these reactions either. However, the reactions of compounds **4** with CN^tBu proceed at a somewhat lower rate, which allows a stoichiometric control of the reaction. When 1 equiv of CN^tBu is used, the isocyanide-bridged species $[Mo_2L_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-}dppm)]$ (**6a**, L = Cp; **6b**, L = Cp′) (Chart 4) are formed in good yields. The structural characterization of compounds **6** is straightforward by comparison of their spectroscopic data with those of the ditungsten analogue $[W_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-}dppm)]$[1] or the related species $[W_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CNR)(CO)_4]$ (R = ^{t}Bu, Ph, Me)[14] and $[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_3(\eta^1\text{-}dppm)]$.[15] In particular, the coordination of the isocyanide ligand in a σ, π fashion is deduced from the low C−N stretching frequencies (*ca.* 1670−1640 cm^{-1}) and high ^{13}C NMR chemical shifts (223 ppm for **6a**). We must note that for compounds **6** two C−N stretches (instead of a single one) are observed in the IR spectrum. This has been found sometimes for either terminal[16] or bridging[15] isocyanide ligands and might be attributed to the presence of more than one conformer for these molecules.

The ditungsten analogue of compounds **6** was found to isomerize at room temperature to yield the corresponding hydrido cyclopentadienylidene complex $[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_2(CN^tBu)(\mu\text{-}dppm)]$.[1] Indeed complexes **6** also have only a moderate stability; however they do not experience C−H(cyclopentadienyl) cleavage processes at a significant extent. Instead, the isocyanide ligand dissociates rather easily (for example during the usual purification steps) so that the corresponding dicarbonyls **4** are regenerated. In spite of this, we note that the ^1H NMR spectra of crude samples of the methylcyclopentadienyl complex **6b** denote the presence of small amounts of a species having a hydrido resonance at −12.35 ppm (dd, J_{PH} = 41, 26 Hz). This could well correspond to a hydrido cyclopentadienylidene complex analogous to the above mentioned ditungsten compound. However, no conditions could be found for increasing the relative amount of this minor species.

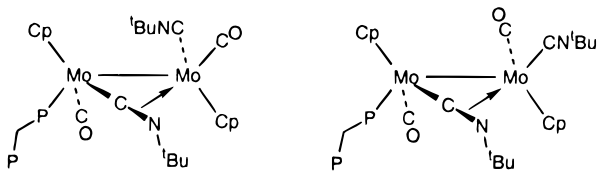


Figure 1. Proposed structures for the isomers detected in the solutions of complex **7** (P−P = dppm).

Compound **6a** reacts slowly with an excess of CN^tBu at room temperature to afford the bis(isocyanide) complex $[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CN^tBu)(CO)_2(\eta^1\text{-}dppm)]$ (**7**). Although the crude reaction mixture contained no other organometallic products in significant amounts (as shown by IR and ^{31}P NMR spectroscopy), all attempts to isolate this complex as a pure solid sample were unsuccessful. In fact, rapid decomposition of this species takes place when the excess isocyanide ligand is removed. The methylcyclopentadienyl compound **6b** reacts analogously with an excess of CN^tBu, but the product was even less stable and no further attempts were made to characterize it.

The retention of the η^1,η^2-bridging isocyanide in complex **7** is clearly indicated by the presence of C−N stretching bands at 1651 and 1619 cm^{-1}, while the new terminal isocyanide ligand gives rise to a characteristic C−N stretch at 2120 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** suggests the presence of two similar isomers, they being present in a *ca.* 1:1 ratio. Each of these isomers (labeled *A* and *B* in Table 1) gives rise to two doublets, one of them at *ca.* 70 ppm and the other one at *ca.* −25 ppm, the latter being very close to the chemical shift of the free dppm ligand. These data are clearly indicative of the presence of unidentate dppm ligand and are similar to those measured for $[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CN^tBu)(CO)_3(\eta^1\text{-}dppm)]$.[15] In fact, the structure of compound **7** can be derived from the molecular structure of the above tricarbonyl complex,[15] after replacing one carbonyl by a terminal CN^tBu ligand. As the latter complex presents no isomers in solution, those isomers observed for compound **7** then probably arise from the two possible coordination positions of the terminal isocyanide relative to the bridging one, at the metal atom not bearing the phosphorus ligand (Figure 1).

The formation of compound **7** from **6a** implies that coordination of the second CN^tBu ligand causes a Mo−P cleavage process. This is somewhat unexpected considering the lability of the bridging isocyanide ligand in **6** and the fact that the related complexes $[Mo_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CNR)(CO)_4]$ (R = ^{t}Bu, Ph, Me) transform into $[Mo_2Cp_2(CNR)_2(CO)_4]$ upon reaction with CNR.[14a] Thus, formation of complex **7** rather than its dppm-bridged isomer $[Mo_2Cp_2(CN^tBu)_2(CO)_2(\mu\text{-}dppm)]$ might have an steric origin, as the relatively bulky dppm ligand thus occupies a less space-demanding position.

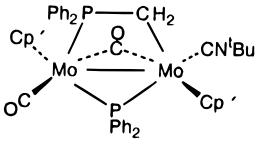
Reactions of Compounds 2 and 5 with CO and CN^tBu. In order to trace back the decarbonylation pathway leading from compounds **1** to **2** or **5**, we decided to study the carbonylation reactions of the latter unsaturated species. This also should give us information about the reversibility of the P−C cleavage process

(14) (a) Adams, H.; Bailey, N. A.; Bannister, C.; Faers, M. A.; Fedorko, P.; Osborn, V. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 341. (b) Adams, R. D.; Katahira, D. A.; Wang, L. W. *Organometallics* **1982**, *1*, 231.

(15) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *382*, 407.

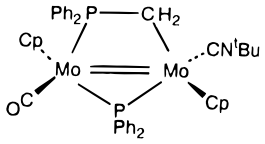
(16) (a) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (b) Harris, G. W.; Albers, M. D.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1983**, *2*, 609. (c) Riera, V.; Ruiz, J.; Jeannin, Y.; Philoche-Levisalles, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1591. (d) Martínez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1988**, *340*, 187.

Chart 5

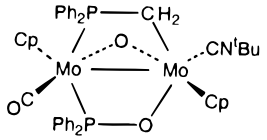


8

Chart 6



9



10

responsible for the formation of these products. Once again, CN^tBu was also used as a model for CO when the latter gave not enough information.

As expected, the triply-bonded monocarbonyls **5** react rapidly with CO (1 atm) at room temperature to give quantitatively the corresponding dicarbonyls **2**. Surprisingly, however, the reaction does not proceed any further under these conditions, in spite of the formal unsaturation of complexes **2**. We noticed that toluene solutions of **2a** changed from brown to pink upon exposure to a higher CO pressure (*ca.* 2−3 atm), but the change was reversed as soon as the pressure was released.

In an attempt to model the carbonylation reaction of dicarbonyls **2** we reacted **2b** with 1 equiv of CN^tBu, this ligand being a better electron donor than CO. That reaction proceeds rapidly in THF at 0 °C to give almost quantitatively the isocyanide complex $[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(\mu\text{-}CO)(CO)]$ (**8**) (Chart 5). Compound **8** can be isolated as an essentially pure solid, but attempts to further purify it led to its progressive (crystallization) or complete (chromatography) decomposition. The oxo complex **3b** was found as a major species in these attempts, which suggests that the isocyanide ligand in **8** is labile.

The spectroscopic data for **8** show ^1H and ^{31}P NMR resonances for the phosphido and phosphinomethyl groups not very different from those of **2b**. The IR spectrum of **8** clearly indicates that the isocyanide ligand adopts a terminal coordination mode ($\nu_{st}(CN) = 2130\ cm^{-1}$) while one of the carbonyls has moved into a bridging position ($\nu_{st}(CO) = 1685\ cm^{-1}$). This is further corroborated in the ^{13}C NMR spectrum, which shows respectively low (163.2 ppm) and high (294.4 ppm) chemical shifts for the coordinated carbon atoms of these ligands. In addition, the terminal carbonyl ($\delta_C = 256.6$ ppm) is equally coupled to both phosphorus atoms ($J_{PC} = 16$ Hz) while the coordinated carbon of the isocyanide ligand is just coupled to a single phosphorus atom. This strongly suggests that the isocyanide ligand is bonded to the molybdenum atom bearing the C-end of the phosphinomethyl group.

The regiospecific addition of CN^tBu to **2b** can be attributed to both electronic and steric factors. In the first place, the PPh_2 group of the phosphinomethyl ligand is clearly more space-demanding than its CH_2 group. On the other hand, the former group is also likely to be a somewhat better donor. Thus, coordination of CN^tBu at the CH_2-bonded molybdenum atom in compounds **2** would be favored because this metal atom is both the less crowded and also somewhat electron poorer in the dimetal center.

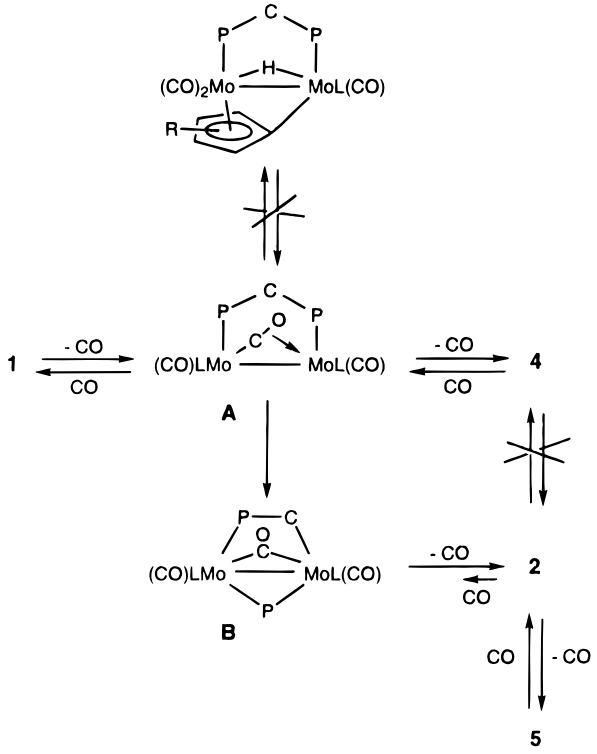
The above considerations should apply for the monocarbonyl compounds **5**, so we would predict that CN^tBu should bind this molecule at the CH_2-bonded molybdenum atom. Unfortunately, direct verification of this hypothesis was not possible. Indeed, complex **5a** reacts rapidly with 1 equiv of CN^tBu to give cleanly $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CN^tBu)(CO)]$ (**9**) (Chart 6), which is isoelectronic to complexes **2**. The ^{31}P NMR spectrum of **9** is similar to that of **2a** as expected, while its IR spectrum denotes the presence of terminal isocyanide ($\nu_{st}(CN) = 2040\ cm^{-1}$) and carbonyl ($\nu_{st}(CO) = 1760\ cm^{-1}$) ligands. However, complex **9** is extremely air sensitive, so we could not assign unambiguously its ^1H NMR resonances nor obtain an informative ^{13}C NMR spectrum. Thus, direct identification of the coordination position of the isocyanide ligand in this species could not be achieved.

Reaction of complex **9** with molecular oxygen gives with good yield the oxo derivative $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}O)(\mu\text{-}OPPh_2)(CN^tBu)(CO)]$ (**10**). This complex is isoelectronic and presumably isostructural to the dicarbonyl compound $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}O)(\mu\text{-}OPPh_2)(CO)_2]$.[9] In fact, ^1H, ^{31}P, and ^{13}C NMR data for these two species are very similar and need then no further discussion. The location of the terminal isocyanide in **10** is determined on the basis of the observed P−C couplings. Thus, the terminal carbonyl gives rise to a doublet of doublets in the ^{13}C NMR spectrum at 254.1 ppm ($J_{PC} = 17$, 14 Hz), which safely places it on the molybdenum atom bearing both phosphorus atoms of the molecule. Therefore, the isocyanide ligand in **10** must be located at the metal atom bearing the CH_2- and O-ends of the bridging groups. This is consistent with the fact that this ligand gives rise to a singlet ^{13}C NMR resonance at 174.4 ppm, because at that position there are only three-bond pathways connecting the isocyanide carbon with any of the phosphorus atoms of the molecule, and this is expected to result in very small P−C couplings. On the other hand, as there is no reason to anticipate a change in the location of the terminal isocyanide ligand when going from **9** to **10**, it is assumed that this ligand in compound **9** is also bonded to the metal atom bearing the C- and O-ends of the bridging phosphorus ligands (Chart 6), in agreement with the initial expectations.

The formation of the oxo complex **10** requires the addition of an oxygen atom to the double metal−metal bond in **9** and insertion of a second oxygen in a P(phosphido)−metal bond, specifically in that metal atom bonded to the CH_2 group of the phosphinomethyl ligand. This insertion pattern parallels that found for the reactions of **2a** with molecular oxygen[9] and can be understood on grounds similar to the ones used above to rationalize the reactions of complexes **2** or **5** toward CN^tBu. As a result, the phosphido group is transformed into a bridging phosphidoxo (μ-$OPPh_2$) ligand. Precedents for this insertion reactions are scarce, but some examples are available from studies on group 9 metal dimethylphosphido complexes.[17] Alternatively, P−C

(17) (a) Klingert, B.; Rheingold, A. L.; Werner, H. *Inorg. Chem.* **1988**, *27*, 1354. (b) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

Scheme 1. Proposed Reaction Pathways in the Decarbonylation Reactions of Compounds 1[a]



[a] L = C_5H_4R; R = H, Me; P−C−P = $Ph_2PCH_2PPh_2$.

cleavage reactions in tertiary phosphine oxides also represent a potential synthetic route for this sort of complex.[18]

Reaction Pathways in the Decarbonylation of Compounds 1. We have shown above that, depending on the particular reaction conditions, the decarbonylation reactions of complexes **1** can lead to one or several of the products **2**, **4**, and **5**, the results being rather insensitive to the nature of the cyclopentadienylic ring (Cp or Cp′). In addition, the reactions of these unsaturated products with CO and CN^{t}Bu provide complementary information about the nature and structure of the intermediates likely involved. All these data allow us to propose a general mechanism which gives a satisfactory explanation of the decarbonylation reactions experienced by the dimolybdenum complexes **1** (Scheme 1).

As proposed for the ditungsten analogues of compounds **1**, the first step would be the ejection of a CO molecule to yield a tricarbonyl intermediate **A**. The latter would probably have a μ-η^1,η^2-CO ligand, by analogy with the related compounds [$M_2Cp_2(\mu$-η^1,η^2-CO)$(CO)_4$], which have been detected in PVC or frozen gas matrixes as primary products in the photolysis of the hexacarbonyl complexes [$M_2Cp_2(CO)_6$].[19] Intermediate **A** is also isostructural to the isocyanide-bridged complexes **6** and would experience two major processes: (a) a reversible further decarbonylation, yielding the triply-bonded complexes **4** or (b) an intramolecular but irreversible P−C(sp^3) oxidative addition of the dppm ligand to yield intermediate **B**. The latter is isostructural to the isocyanide complex **8** and would easily decarbonylate further to yield the dicarbonyls **2**. We recall here that complexes **2** give no stable CO adducts (*i.e.* intermediates **B**) and that compound **8** easily gives up the isocyanide ligand. Thus, the equilibrium **B**/**2** + CO seems to be shifted far to the right under the experimental conditions examined. Finally, compounds **2** would lose under photochemical activation (but not upon heating) a further CO molecule to yield the monocarbonyls **5**, as it has been demonstrated through separate experiments.

From our data it is clear that processes a and b can occur both under thermal or photochemical conditions but at different extents. We recall here that the corresponding products, **4** and **2** (or **5**), do not interconvert under these conditions, so the product distribution is kinetically controlled. Thus, P−C cleavage of the backbone of the dppm ligand becomes dominant (faster) at high temperatures (thermal decarbonylations in the range 65−110 °C) while it is fairly well suppressed at low temperatures (photochemical decarbonylations at 10 °C or below). This is not surprising, as the vast majority of observed P−C cleavage processes in phosphine ligands occur upon heating.[3] This is also the case for the P−C(sp^3) cleavages occurring on the diiron complexes [$Fe_2(\mu$-CO)$(CO)_6(\mu$-$R_2PCH_2PR_2)$],[20] which are entirely analogous to the ones here reported.

In the light of our previous studies on the ditungsten analogues of **1**,[1] we would have expected to observe the products of a third reaction pathway starting from intermediate **A**, that is the intramolecular C−H (Cp) oxidative addition leading to the hydride [$Mo_2(\mu$-η^1,η^5-$C_5H_3R)(\eta^5$-$C_5H_4R)(\mu$-H$)(CO)_3(\mu$-dppm)] (R = H, Me). However, as we have said above, we have obtained only weak evidence for the presence of this type of product, which in any case are formed in very small amounts. This stands in contrast to the behavior of the ditungsten system, where the C−H cleavage process can be entirely dominant. There is no clear explanation for that significant difference when moving from molybdenum to tungsten. In our studies on the photochemical decarbonylations of [$M_2Cp_2(CO)_6$] (M = Mo, W) we have established that C−H (Cp) cleavages invariably occur to yield the trinuclear clusters [$M_3(\mu$-η^1,η^5-$C_5H_4)Cp_2$-$(CO)_6$].[21] From these studies we concluded that the cyclopentadienylidene ligand has a marked thermodynamic preference to form σ bonds to tungsten rather than to molybdenum atoms. So this thermodynamic effect could be in part responsible for the evolution of the dimolybdenum intermediate **A** *not* through the C−H cleavage pathway. Another effect working in favor of the P−C cleavage pathway is the fact that the transformation **A** into **B** seems to be irreversible, while the C−H cleavage of the cyclopentadienylic ring is expected to be reversible.[1]

The above considerations allow us to partially understand why the dimolybdenum systems evolve through P−C rather than C−H bond cleavage pathways. However, it remains unclear why the P−C cleavage of the

(18) Fogg, D. E.; Taylor, N. J.; Meyer, A.; Carty, A. J. *Organometallics* **1987**, *6*, 2252.

(19) (a) Hooker, R. H.; Rest, A. J. *J. Organomet. Chem.* **1983**, *254*, C25. (b) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, *1221*. (c) Baker, M. L.; Bloyce, P. E.; Campen, A. K.; Rest, A. J.; Bitterwolf, T. E. *Ibid.* **1990**, 2825.

(20) (a) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Morton, D. A. V.; Orpen, A. G. *Inorg. Chim. Acta* **1992**, *198−200*, 257. (b) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 540.

(21) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1324.

backbone of the dppm ligand remains a relatively efficient process for the dimolybdenum complex **1** even at 10 °C (photochemical decarbonylations) while for the ditungsten analogues this process is almost absent under all decarbonylation conditions examined (thermal or photochemical). Further experiments on the mixed-metal (MoW) analogues of the tetracarbonyl species **1** are currently under way, which are expected to provide some useful complementary information concerning this matter.

Experimental Section

General Comments. The general experimental techniques and manipulation procedures are described in ref 1a. The compounds **1a**,[5] $[Mo_2Cp'_2(CO)_4]$,[22] and dppm[23] were prepared as described previously. NMR spectra were recorded at 291 K and 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}), unless otherwise stated. Chemical shifts are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (J) are given in hertz. Complexes **2**, **4a**, **5**, and **9** are highly air-sensitive, and satisfactory elemental analyses could not be obtained in these cases.

Preparation of $[Mo_2Cp'_2(CO)_4(\mu\text{-dppm})]$ (1b). The procedure is totally analogous to that described for **1a**[5] but using $[Mo_2Cp'_2(CO)_4]$ instead of $[Mo_2Cp_2(CO)_4]$. Typical yields on a 5 mmol scale were about 85%. Anal. Calcd for $C_{42}H_{38}Cl_2Mo_2O_4P_2$, **1b**·$CH_2Cl_2$: C, 54.16; H, 4.11. Found: C, 54.63; H, 4.47. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 243 K): δ 7.8−7.1 (Ph), 5.53, 5.29, 5.04, 4.96 (4 × m, 4 × 2H, C_5H_4, isomer *B*), 4.37 (t, J_{PH} = 8, 2H, CH_2, isomer *B*), 2.04 (s, 6H, Me, isomer *B*), 5.04, 4.98, 3.82, 3.56 (4 × m, 4 × 2H, C_5H_4, isomer *A*), 5.28 (t, J_{PH} = 8, 2H, CH_2, isomer *A*), 1.62 (s, 6H, Me, isomer *A*). Ratio *B*:*A* *ca*. 15.

Preparation of $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (2a). A tetrahydrofuran (THF) solution (30 mL) of **1a** (0.819 g, 1.0 mmol) was stirred at 60 °C for 6 h to give a dark brown solution. The solvent was then removed under vacuum and the residue dissolved in toluene and chromatographed at 10 °C on an alumina column (activity 4, 10 × 3 cm) prepared in petroleum ether. Elution with the latter solvent gave a pink fraction containing trace amounts of unidentified species as well as some $[Mo_2Cp_2(CO)_6]$. Elution with toluene gave a brown fraction. Removal of solvents under vacuum from the latter and washing of the residue with petroleum ether yielded complex **2a** as a brown, very air-sensitive powder (0.580 g, 76%). ^{1}H NMR (C_6D_6): δ 8.0−7.1 (20H, Ph), 4.81 (s, 5H, Cp), 4.75 (s, 5H, Cp), 2.61 (dd, J_{HH} = 11, J_{HP} = 4, 1H, CH_2), 1.99 (ddd, J_{HH} = 11, J_{HP} = 17, 3, 1H, CH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 233.0 (t, J_{PC} = 14, CO), 231.6 (dd, J_{PC} = 18, 3, CO), 148.0 − 127.8 (Ph), 91.4, 89.8 (2 × s, Cp), 1.0 (d, J_{PC} = 8, CH_2).

Further elution with toluene gave a violet fraction containing a small amount of the oxo complex **3a**. Finally, elution with toluene−dichloromethane (2:1) gave a green band which, after similar workup, yielded complex **4a** as a green powder (0.040 g, 5%).

Preparation of $[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (2b). A toluene solution (15 mL) of **1b** (0.200 g, 0.24 mmol) was stirred at 110 °C for 45 min while bubbling nitrogen gently through the solution. The resulting brown mixture was concentrated under vacuum to *ca*. 5 mL and then chromatographed at 10 °C on an alumina column (activity 3.5, 20 × 2.5 cm) prepared in petroleum ether. Elution with the latter solvent gave a pink fraction containing a small amount of $[Mo_2Cp'_2(CO)_6]$. Elution with toluene−petroleum ether (7:3) gave a brown fraction. Removal of solvents under vacuum from this fraction yielded complex **2b** as a dark-brown, very air-sensitive microcrystalline powder (0.150 g, 80%). ^{1}H NMR (200.13 MHz, toluene-d_8): δ 8.1−7.1 (20H, Ph), 5.33, 5.22, 5.07, 4.95, 4.85, 4.50, 4.45, 4.07 (8 × m, 8 × 1H, C_5H_4), 2.53 (dd, J_{HH} = 11, J_{PH} = 4, 1H, CH_2), 1.84 (ddd, J_{HH} = 11, J_{PH} = 17, 3, 1H, CH_2), 1.43, 0.98 (2 × s, 2 × 3H, Me).

Elution with toluene gave a violet fraction which yielded, after removal of solvents under vacuum, the oxo complex **3a** as a dark violet powder (0.010 g, 5%). Anal. Calcd for $C_{38}H_{36}Mo_2O_2P_2$, **3b**: C, 58.63; H, 4.66. Found: C, 58.35; H, 4.51. ^{1}H NMR (C_6D_6): δ 8.0−7.0 (20H, Ph), 5.78, 5.18, 5.00, 4.82, 4.65, 4.37, 4.17, 4.12 (8 × m, 8 × 1H, C_5H_4), 3.13 (td, J_{HH} = 11, J_{PH} = 11, 4, 1H, CH_2), 2.29 (dd, J_{HH} = 11, J_{PH} = 6, 1H, CH_2), 1.80, 1.55 (2 × s, 2 × 3H, Me).

Finally, elution with toluene−dichloromethane (4:1) gave a green fraction which, after similar workup, yielded complex **4b** as a green powder (0.015 g, 8%).

Preparation of $[Mo_2Cp_2(CO)_2(\mu\text{-dppm})]$ (4a). A THF solution (15 mL) of compound **1a** (0.082 g, 0.1 mmol) was photolyzed with visible−UV light in a quartz Schlenk tube at 10 °C for 5 h, while bubbling nitrogen gently through the solution. Solvent was then removed under vacuum from the dark green resulting solution, and the residue was washed with toluene−petroleum ether (1:1, 2 × 8 mL) to remove a small amount of compound **5a** in the reaction mixture. The washed residue was dissolved in THF and filtered. Removal of solvent under vacuum from the filtrate yielded compound **4a** as dark green, very air-sensitive solid (0.061 g, 80%). ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 7.50−7.10 (20H, Ph), 5.29 (t, J_{HP} = 10, 2H, CH_2), 4.51 (s, 10H, Cp). ^{13}C{^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 254.2 (t, J_{CP} = 5, CO), 138.4 (false t, J_{CP} + $J_{CP'}$ = 45, C^1[Ph]), 133.0 (false t, J_{CP} + $J_{CP'}$ = 12, Ph), 129.8 (s, C^4[Ph]), 128.3 (false t, J_{CP} + $J_{CP'}$ = 10, Ph), 89.1 (s, Cp), 63.7 (t, J_{PC} = 22, CH_2).

Preparation of $[Mo_2Cp'_2(CO)_2(\mu\text{-dppm})]$ (4b). Complex **1b** (0.150 mg, 0.18 mmol) was photolyzed as described above during 6 h. After removal of the solvent under vacuum, the residue was dissolved in the minimum amount of toluene and chromatographed at 10 °C on an alumina column (activity 3.5, 20 × 2.5 cm) prepared in petroleum ether. Elution with toluene−dichloromethane (5:1) gave a green fraction which yielded, after removal of solvents under vacuum, complex **4b** as a dark green, air-sensitive microcrystalline solid (0.105 g, 75%). Elution with toluene−dichloromethane (3:1) gave a gray fraction which yielded, after similar workup, complex **5b** as a dark gray microcrystalline solid (0.020 g, 15%). Anal. Calcd for $C_{39}H_{36}Mo_2O_2P_2$, **4b**: C, 59.25; H, 4.59. Found: C, 58.53; H, 4.74. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 7.5−7.1 (20H, Ph), 5.29 (t, J_{PH} = 10, 2H, CH_2), 4.50, 3.93 (2 × m, 2 × 4H, C_5H_4), 2.01 (s, 6H, Me). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2): δ 254.6 (s, br, CO), 138.3 (false t, J_{CP} + $J_{CP'}$ = 46, C^1[Ph]), 133.0 (false t, J_{CP} + $J_{CP'}$ = 12, Ph), 129.1 (s, C^4[Ph]), 128.2 (false t, J_{CP} + $J_{CP'}$ = 9, Ph), 105.6 (s, C^1[C_5H_4]), 89.6, 87.8 (2 × s, C_5H_4), 63.7 (t, J_{PC} = 22, CH_2), 14.4 (s, Me).

Preparation of $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-CO})]$ (5a). Complex **2a** (0.077 g, 0.1 mmol) was photolyzed as described above for 1 h to give a black-blue solution. Solvent was then removed under vacuum, the residue extracted with toluene−petroleum ether (1:1) (2 × 10 mL) and filtered. Removal of solvents from the filtrate yielded complex **5a** as a highly air-sensitive solid (0.070 g, 95%). ^{1}H NMR (toluene-d_8): δ 7.23−6.70 (20H, Ph), 5.27 (d, J_{HP} = 1, 5H, Cp), 4.97 (s, 5H, Cp), 0.03 (ddd, J_{HH} = 11, J_{PH} = 6, 1, 1H, CH_2), −0.42 (dd, J_{HH} = 11, J_{PH} = 8, 1H, CH_2). ^{13}C{^{1}H} NMR (toluene-d_8): δ 304.5 (t, J_{PC} = 16, μ-CO), 153.6−124.4 (Ph), 95.8, 94.1 (2 × s, Cp), and −13.4 (s, CH_2).

Preparation of $[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-CO})]$ (5b). Complex **2b** (0.065 g, 0.08 mmol) was photolyzed as described above for 75 min to give a black solution. Workup as described for **5a** yielded compound **5b** as a dark-gray, highly air-sensitive solid (0.057 g, 90%). ^{1}H NMR (C_6D_6): δ 7.3−6.8 (20H, Ph), 5.50, 5.18, 4.93, 4.76, 4.42 (5 × m, 5 × 1H, C_5H_4),

(22) Curtis, M. D.; Klinger, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

(23) Agiar, A. M.; Beisler, J. *J. Org. Chem.* **1964**, *29*, 1660.

5.10−5.05 (m, 3H, C_5H_4), 1.82, 1.79 (2 × s, 2 × 3H, Me), −0.06 (ddd, J_{HH} = 11, J_{PH} = 6, 1, 1H, CH_2), −0.40 (dd, J_{HH} = 11, J_{PH} = 8, 1H, CH_2). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 305.7 (br, μ-CO), 153.5−125.5 (Ph), 111.8, 108.7 (2 × s, $C^1[C_5H_4]$), 96.7, 95.6, 95.5, 94.9, 94.7, 93.1, 92.0, 91.8 (8 × s, C_5H_4), 14.4, 13.7 (2 × s, Me), −9.5 (s, CH_2).

Preparation of [$Mo_2Cp_2(\mu$-η^1,η^2-CN^{t}Bu)(CO)$_2(\mu$-dppm)] (6a). A THF solution (8 mL) of compound **4a** (0.038 g, 0.05 mmol) was stirred with CN^{t}Bu (6 μL, 0.05 mmol) at room temperature for 5 min, whereupon its color changed from green to red-brown. Solvent was then removed under vacuum at 0 °C and the residue dissolved in toluene (10 mL) and filtered. Removal of solvent under vacuum from the filtrate at 0 °C and washing of the residue with petroleum ether at the same temperature (2 × 3 mL) yielded compound **6a** as a brown solid (0.039 g, 92%). Anal. Calcd for $C_{42}H_{41}Mo_2NO_2P_2$, **6a**: C, 59.65; H, 4.89; N, 1.66. Found: C, 60.15; H, 4.91; N, 1.82. ^1H NMR (200.13 MHz, toluene-d_8): δ 8.40−6.80 (20H, Ph), 5.48 (t, J_{PH} = 9, 2H, CH_2), 4.60 (d, J_{HP} = 2, 5H, Cp), 4.22 (s, 5H, Cp), 1.39 (s, 9H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 238 K): δ 261.9 (d, J_{PC} = 29, CO), 241.5 (d, J_{PC} = 15, CO), 223.1 (s, μ-*C*NCMe$_3$), 145.0−127.0 (Ph), 93.4, 90.6 (2 × s, Cp), 59.0 (s, μ-CN*C*Me$_3$), 31.2 (s, Me). The resonance due to the CH_2 group is obscured by that one from the solvent.

Preparation of [$Mo_2Cp'_2(\mu$-η^1,η^2-CN^{t}Bu)(CO)$_2(\mu$-dppm)] (6b). The procedure is completely analogous to that described for **6a** but using dichloromethane as solvent. This compound was found to decompose in solution or in the solid state (especially under vacuum) more rapidly than complex **6a** so that a satisfactory ^1H NMR spectrum or elemental analysis could not be obtained.

Preparation of Solutions of [$MO_2Cp_2(\mu$-η^1,η^2-CN^{t}Bu)(CN^{t}Bu)(CO)$_2(\eta^1$-dppm)] (7). A THF (8 mL) solution of complex **6a** (0.043 g, 0.05 mmol) was stirred with CN^{t}Bu (18 μL 0.15 mmol) at room temperature for 24 h to afford a brown solution. The latter was shown (by ^{31}P NMR) to contain only two (presumably) isomers of **7** in a *ca*. 1:1 ratio (see Discussion). Decomposition of these species rapidly occurs when the excess isocyanide is removed from the solution (vacuum, crystallization, etc.).

Preparation of [$Mo_2Cp'_2(\mu$-$CH_2PPh_2)(\mu$-$PPh_2)$(CN^{t}Bu)(μ-CO)(CO)] (8). A THF solution (12 mL) of compound **2b** (0.085 g, 0.1 mmol) was stirred with CN^{t}Bu (13 μL, 0.1 mmol) at 0 °C for 10 min to give an orange solution which was filtered. Removal of solvents under vacuum from the filtrate and washing of the residue with petroleum ether (2 × 5 mL) yielded essentially pure compound **8** as an orange powder (0.080 g, 85%). Further purification of this compound could not be achieved (see Discussion). ^1H NMR (400.13 MHz, CD_2Cl_2, 253 K): δ 7.7−6.9 (20H, Ph), 4.81, 4.76, 4.47, 4.39, 4.36, 4.31, 3.60, 3.35 (8 × m, 8 × 1H, C_5H_4), 1.92, 1.85 (2 × s, 2 × 3H, Me), 1.37 (t, J_{HH} = J_{PH} = 11, 1H, CH_2), 0.62 (dd, J_{HH} = 11, J_{PH} = 9, 1H, CH_2), 0.54 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 233 K): δ 294.4 (d, J_{PC} = 23, μ-CO), 256.6 (t, J_{PC} = 16, CO), 163.2 [d, J_{CP} = 13, *C*NC(CH$_3$)$_3$], 150.9−124.9 (Ph), 105.5, 104.4 (2 × s, $C^1[C_5H_4]$), 96.8, 96.0, 93.2, 91.4, 88.8, 88.4, 88.2, 87.0 (8 × s, C_5H_4), 55.1 [s, CN*C*(CH$_3$)$_3$], 27.9 [s, CNC-(*C*H$_3$)$_3$], 13.7, 12.4 (2 × s, C_5H_4*C*H$_3$), −14.6 (s, CH_2).

Preparation of [$Mo_2Cp_2(\mu$-$CH_2PPh_2)(\mu$-$PPh_2)$(CN^{t}Bu)(CO)] (9). A THF solution (10 mL) of compound **5a** (0.052 g, 0.07 mmol) was stirred with CN^{t}Bu (8 μL, 0.07 mmol) at 10 °C for 5 min to give a brown-red solution. Solvent was then removed under vacuum and the residue extracted with toluene (2 × 8 mL) and filtered. Removal of solvent from the filtrate under vacuum and washing of the residue with petroleum ether (3 × 3 mL) at 0 °C gave compound **9** as a highly air-sensitive brown powder (0.050 g, 90%).

Preparation of [$Mo_2Cp_2(\mu$-$CH_2PPh_2)(\mu$-O)(μ-OPPh$_2$)(CN^{t}Bu)(CO)] (10). A THF solution (15 mL) of compound **9** (0.070 g, 0.095 mmol) was treated with air (11 mL, *ca*. 0.1 mmol of O_2) under nitrogen and stirred for 10 min to give a brown solution. Solvent was then removed under vacuum and the residue washed with petroleum ether (4 × 4 mL), extracted with toluene (2 × 8 mL), and filtered. Removal of solvent from the filtrate yielded compound **10** as a brown powder (0.057 g, 70%). Anal. Calcd for $C_{41}H_{41}Mo_2NO_3P_2$, **10**: C, 57.96; H, 4.86, N, 1.65. Found: C, 57.52; H, 4.62; N, 1.50. ^1H NMR (200.13 MHz, toluene-d_8): δ 7.9−6.9 (20H, Ph), 4.84 (s, 5H, Cp), 4.77 (t, J_{HP} = 2, 5H, Cp), 2.27 (dd, J_{HH} = 11, J_{PH} = 8, 1H, CH_2), 1.32 (s, 9H, Me), −0.25 (t, J_{HH} = J_{PH} = 11, 1H, CH_2). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 243 K): δ 254.1 (dd, J_{PC} = 17, 14, CO), 174.4 (s, *C*NCMe$_3$), 148.5−128.0 (Ph), 96.2, 94.4 (2 × s, Cp), 58.8 (s, CN*C*Me$_3$), 31.1 (s, Me), 0.2 (s, CH_2).

Acknowledgment. We thank the DGICYT of Spain for financial support (Project PB91-0678).

OM9607154